I. STUDY OF THE STABILITY OF GRAIN ADJUNCTS IN BREWING

II. CRYSTALLIZATION OF WAX-OIL SYSTEMS

BY

HOMER JAMES BIRCH

B.S., Youngstown College, 1941
M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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I. STUDY OF THE STABILITY OF GRAIN ADJUNCTS IN BREWING

Introduction

The relative merits of corn and rice as beer adjuncts have been a matter of controversy for some time. Brewers are divided in their opinions, some using rice exclusively, some corn only and others use blends of the two grains. Those brewers who prefer rice claim that corn adjuncts lower the quality of the beer flavor. They attribute this loss of flavor to rancidity developed in the corn oils extracted into the wort (1). The object of this investigation was to determine whether there are any marked differences in beers prepared from corn as contrasted with those made with rice as an adjunct.

Experimental And Results

The development of rancidity in oils is usually accompanied by the absorption of oxygen with the formation of peroxides along with increase in the free acid content and consequent changes in the absorption spectrum. The determination of peroxides may be made by a number of methods, of which Macarovici (2) has found the most reliable one to be the liberation of iodine from iodide solutions. Determinations made upon samples of freshly extracted oil from rice, corn and malted barley gave low peroxide content in all three, while either exposure to air or to sunlight caused large increases in peroxide content. The results for such determinations are given in Table I as millimoles of peroxide per gram oil.

TABLE I

	New Oil	10 Day Storage	1 Day Irrad.	3 Day Irrad.
Corn	.004	.034	.045	.032
Rice	.003	.052	.088	.046
Malt	.004	.043	.072	.032

Spectrophotometric absorption curves corroborated these changes, indicating lower stability in the rice oil. Worts prepared from 1) fresh, 2) solvent-extracted and 3) irradiated grain had absorption spectra which are in agreement with this relative stability.

Organoleptic tests of beer prepared using corn and rice adjuncts were made, and in a series of samples to which varying quantities of fresh and rancid oil had been added, no definite preference for either grain adjunct was shown. Oil content was detectable in 5 ppm concentration.

Results indicate that little differences exist between rice and corn as brewing adjuncts, although corn oil possesses much more stability to development of rancidity from air and light exposure.

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II. CRYSTALLIZATION OF WAX-OIL SYSTEMS

Introduction

Waxes are derived from a wide variety of sources and have many wide deviations in composition and properties. Their classification as waxes is dependent mainly upon the nature of their solid state, beeswax being taken as the prototype (1). Waxes are used in many products such as pastes, polishes, inks and carbon papers (2,3). In most of these products, wax is blended with other materials to give the desired properties. A coating for paper has been developed in which the wax holds paraffin oil containing dissolved dye. Upon the application of pressure, a portion of the oil is discharged and is absorbed by

another paper surface yielding a copy of the original impression. The release of the applied pressure restores the stable nature of the wax-oil mixture. The phase changes involved in such a process have both practical and theoretical significance.

Experimental And Results

The investigation was confined to four waxes; namely, Gersthofen, Montan, Ouricury and paraffin in the pure state, along with several mixtures containing varying amounts of oil. X-ray methods were used to determine lattice spacings of the pure waxes and the oil-containing mixtures (4). Comparison of the spacings found revealed little or no variation between those of the pure components and mixtures and so no evidence was obtained to indicate solid solution or mixed crystal formation. None of the waxes, with the exception of paraffin, gave long spacings indicative of repetitive units along the carbon chain.

Crystallization studies were made using a Kofler hot stage with an optical microscope, as well as a specially developed filament heater by means of which a temperature gradient could be created across the microscope field. Observation of crystal nucleation under crossed Nicol prisms showed the microcrystalline nature of all of the waxes. Samples containing 55 per cent oil revealed thixotropic properties (5) at temperatures as low as 10°C while with decreasing amounts of oil the temperature at which the thixotropic properties appeared increased.

Surface studies were made of a series of samples using incident-light photomicrographs. The lack of sufficient detail in such pictures led to the development of a replica technique by which electron microscope study of the surfaces was possible. Replicas were made using gold-chromium alloy for shadowing with a backing of beryllium-aluminum alloy. Numerous studies under different conditions of treatment and composition were performed. A large number of such electron

micrographs are included, at magnifications of 13,000 diameters.

The waxes were found to have definite characteristics of surface formation, a lamellate structure being shown by the Ouricury wax. Study of this structure and comparison of it with the structure seen in other mixtures indicate that the waxes crystallize in laminated plates. A wax plate consists of a single layer of molecular chains oriented parallel to each other and perpendicular to the plane of the plate. Oil molecules may enter between plates or penetrate between the molecules in the plate disrupting the orderly laminated structure. This decrease in order lowers the strength of the solid form and causes the plastic state observed in wax pastes. Under stress the regions of lower order are disrupted and become fluid, flowing between the areas of higher crystallinity. The return to the solid state upon release of the applied stress is due to the establishment again of this low ordered state between wax and oil molecules.

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VITA

Homer James Birch was born near Struthers, Ohio, on June 1, 1918. He received his primary and secondary education there, being graduated from Struthers High School in 1935. He entered Youngstown College from which he received the Bachelor of Science degree in June, 1941. While enrolled at Youngstown College, he was employed by Struthers Iron and Steel Co. From 1941 until September, 1948, he was employed in the Works Laboratory of the Ammonia Department of E. I. duPont de Nemours & Co. He resigned from this position to enter the Graduate College of the University of Illinois, from which he received the Master of Science degree in August, 1949. During the academic years 1949-50 and 1951-52 he held a teaching assistantship in the Analytical Division. He was awarded the Lauhoff Grain Co. fellowship in 1950-51. He is a member of Sigma Xi and the American Chemical Society.